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Investigation of Mechanical Stability of Thermally Aged a-c:H DLC Films with Different Precursor Gases

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Abstract. A-C: H (Hydrogenated amorphous carbon) diamond like carbon(DLC) film is the low stabilities of chemical and mechanical properties at high temperatures. Some researchers reported that Raman spectra shown significant conversion of DLC films to nano-crystalline graphite on heating in ambient air at temperatures above 300**°C** and conversion to nano-crystalline graphite was completed by 450~600**°C** In this study, DLC films(thickness : 1.5µm) were deposited on p-type (100) silicon films by using C_6H_6 and C_6H_{14} plasma produced with a 13.6MHz RF source. To investigate the mechanical stability of DLC films below 250**°C**, we thermally aged the films for different aging temperatures (150**°C**, 200**°C**, 250**°C**) and times (0: virgin, 120, 240, 360 hours). By using indentation test and Raman spectra analyses, it has been found that the H^3/E^2 decreases with increasing I(D)/I(G) ratio. Also we confirmed that sample-2(precursor gas: C_6H_{14}) had better mechanical characteristic and thermal stability than the sample-1(precursor gas: C_6H_6).

Introduction

The measurement of thin film material parameter is extremely difficult owing to the small material volumes involved. Ideally, these parameters should be known for process optimization and for coating lifetime engineering. Most studies that have attempted to improve the mechanical properties have either used tests under service conditions or test procedures simultaneously involving several mechanical properties. The identification of the crucial material parameters, however, is not straightforward in such situations and engineering of film-substrate systems remains difficult [1].

Generally, the DLC films have a mixed sp3/sp2 structure with different proportions of sp^3 and sp^2 bonds depending on the deposition techniques and deposition parameters used. Accordingly, the material property of DLC films can differ considerably depending on the deposition method, hydrocarbon source gas and deposition parameters used. The deposited diamond like carbon (DLC) film has advantageous mechanical and chemical properties such as high wear resistance, high hardness, and low friction, which can guarantee the good condition of coating against wear and fracture [2]. Thermo-mechanical loads in the film-substrate compound are caused by the non-uniformity of the temperature field and by the difference of the material properties of substrate and film. The loading can result in cracking, delamination or spalling of the protective layer, which limits the coating lifetime [3].

In this study, DLC films(thickness : 1.5µm) were deposited on p-type (100) silicon films by using C_6H_6 and C_6H_{14} plasma produced with a 13.6MHz RF source. To investigate the mechanical stability of DLC films below 250°C with various thermal aging conditions, we thermally aged the films for different aging temperatures (150°C, 200°C, 250°C) and times (0: virgin, 120, 240, 360 hours). The material properties of the aged DLC specimens were investigated by using nano-indentation and Raman analysis.

Table 1 Material properties of DLC and silicon wafer

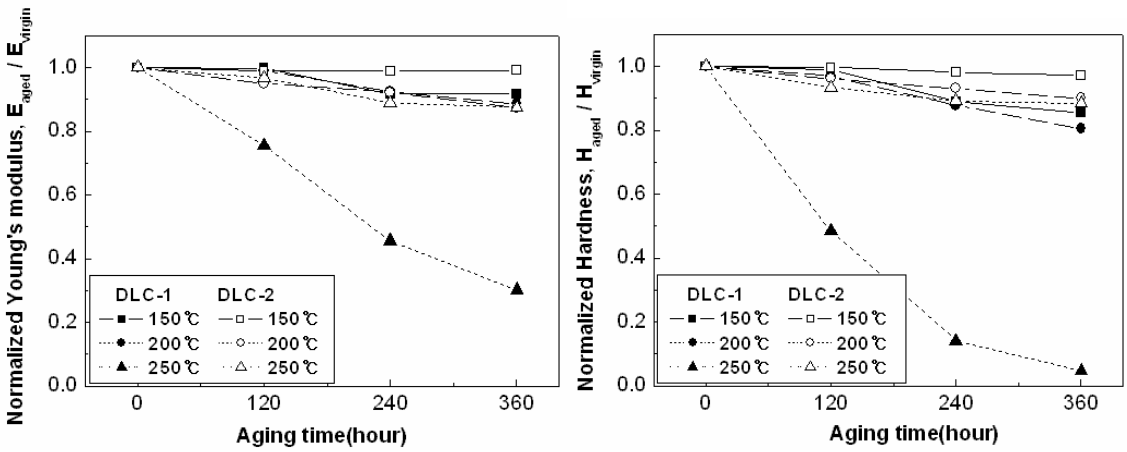
Sample	Si substrate	Sample-1	Sample-2
Source gas	-	Benzene	Hexane
Residual Stress (GPa)	-	1.028	2.695
Thickness	0.3mm	1.5μm	1.5μm

Specimen and test method

DLC films were deposited on p-type Si (100) wafers. Before deposition, the substrates were sputter-cleaned with argon at 3.7mTorr for 15 minute to remove native oxides on the surface. The sputter cleaned samples were then implanted with amorphous silicon using SiH_4 (Silicon hydride) plasma at 10mTorr to create an interlayer (thickness: 10nm) and to improve the adhesion of the a-c:H/single crystalline silicon layer. DLC films were deposited by using C_6H_6 and C_6H_{14} plasma produced with a 13.6MHz RF source. In RF PACVD, the films were deposited at a negative bias voltage of 400V at a deposition pressure of 10mTorr. Because these films have a high content of hydrogen, the films are also referred to as hydrogenated amorphous carbon.

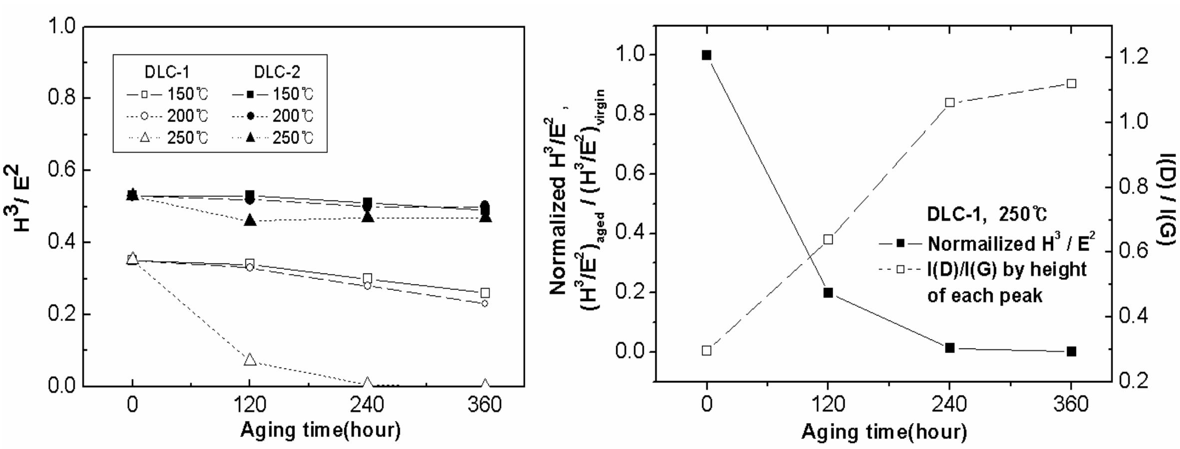
DLC on silicon and single crystalline silicon specimens, about 1.5×1.5cm^2 in size, were cut from a DLC on silicon specimen and uncoated silicon. A summary of the coating thickness and the residual stress of the samples synthesized in this work are presented in Table 1. The thickness of the deposited films was measured by profilometry. Residual stress, which developed in the DLC coatings during the deposition process, was calculated by measuring the radius of curvature of the silicon substrate before and after deposition and employing the Stoney's equation [4].

Indentation experiments were conducted with a fully calibrated Nano Indenter XP. Nano-indentations were made in arrays with the indents spaced apart by at least 10 times the indentation diameter so that interaction of the residual stress fields of neighboring indents would not affect the results. Raman spectroscopy has been performed on virgin and aged samples. Raman spectra obtain by using an argon ion laser operating at a wavelength of 514.50nm are required.



(a) Normalized Young's modulus (b) Normalized Hardness

Fig. 1 Normalized material properties of aged a:C-H DLC films measurement by nano-indentation with various aging time and temperature. (Test temperature: 25°C)



(a) (b)

Fig. 2 H^3/E^2 and Raman intensity ratio with various aging conditions, (a) H^3/E^2 vs aging time, (b) normalized plastic deformation resistance versus Raman intensity ratio, normalized H^3/E^2 vs I(D) / I(G)

Results and discussion

Figure 1 shows the change of the normalized Young's modulus and nano-hardness of the samples with thermal aging, respectively. The material properties of the DLC-2(precursor gas: C_6H_{14}) at 250°C such as Young's modulus, nano-hardness and H^3/E^2 are retained within the 13% of virgin material properties. But, these properties of sample-1 at 250°C decreased much more than those of sample-2, as shown in Figs. 1. The results revealed that sample-2 film (precursor gas: C_6H_{14}) had better mechanical characteristics and thermal stabilities than sample-1 film (precursor gas: C_6H_6).

The information about the structure of aged DLC films was obtained by using Raman spectroscopy. Spectra were measured in the range from 500 to 2000 cm^{-1}. For quantitative analysis, the Raman spectra of all samples were fitted to two Gaussian peaks denoted as the D and the G peak. Generally, G-band means graphite structure located at approximately 1530-1580 cm^{-1}. The increases of the intensity ratio I(D)/I(G) can be ascribed to the decrease of the crystal size[5]. Musil proposed that the ratio H^3/E^2 characterizing the resistance of the material to plastic deformation. The ratio is a parameter which controls resistance of materials to plastic deformation [6].

Figure 2(b) shows the change of the normalized H^3/E^2 and intensity ratio I(D)/I(G) of the aged DLC-1 samples with thermal aging time at 250°C. As can be seen that with increasing of I(D)/I(G), the normalized H^3/E^2 move to a lower ratio. For the virgin specimen of DLC-1, the H^3/E^2 was located at 0.35. With increasing of aging time, the plastic deformation resistance of sample-1 decreased from 0.35 to 0.007 at 250°C in Fig. 2(a). This phenomenon reflects the progress of graphitization of the DLC-1 specimen because increasing I (D)/I(G) is assigned to sp^2 bonded carbon which seems to be aromatic in structure. We also known that increasing I(D)/I(G) ratio is inversely proportional to the decreasing H^3/E^2 ratio of the aged a-C:H DLC-1 film. By comparing these tendencies of the aged a-C:H DLC samples, we confirmed that DLC-2(precursor gas: C_6H_{14}) have better thermal stabilities and mechanical characteristics than DLC-1(precursor gas: C_6H_6).

Conclusion

DLC films have been deposited by PACVD with two different precursor gases, C_6H_6 and C_6H_{14}. The nano-indentation test and the Raman spectra analysis were performed to evaluate the thermal and mechanical stabilities of these films below 250°C. The material properties of the DLC-2(precursor gas: C_6H_{14}) such as Young's modulus, nano-hardness and H^3/E^2 are retained within the 13% of virgin material properties below 250°C (aging time: 360hours). But, the material properties and I(D)/I(G) ratio of Sample-1 dramatically changed. By comparing these tendencies of the aged a-C:H DLC samples, it is confirmed that DLC-2(precursor gas: C_6H_{14}) have better thermal stabilities and mechanical characteristics than DLC-1(precursor gas: C_6H_6).

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